

SURFACE MODIFICATION OF LOW COST CARBONS FOR THEIR APPLICATION IN THE ENVIRONMENTAL PROTECTION

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Abstract

In this work, the CO₂ capture capacity of a series of activated carbons derived from recycled polyethylene terephthalate (PET) was tested, facing two problems at the same time: minimising plastic waste and developing an adsorbent for CO₂ capture. The PET raw material, obtained from post-consumer soft-drink bottles, was chemically activated with KOH. In addition, a series of nitrogen-enriched activated carbons was obtained by mixing the raw material with different nitrogen compounds (i.e., acridine, carbazole and urea). The influence of temperature on the CO₂ capture capacity of the adsorbents was evaluated in a thermogravimetric system. The CO₂ uptake was also related to the chemical and textural characteristics of the samples.

Keywords: CO₂ capture, Carbon materials, Plastic waste, Adsorption

Introduction

Activated carbons are widely used as adsorbents of gases and vapours [1]. In physical adsorption the size and volume of pores are important, thus microporous carbons are used for the sorption/separation of light gases, whereas carbons with broad pore sizes are applied for removal of toxins or other large organic molecules [1, 2]. However, when specific interactions of adsorbate/adsorbents play a role in the adsorption process,

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other features of activated carbons such as surface chemistry should also be taken into consideration [2-4].

The surface chemistry of activated carbons is governed by the presence of heteroatoms such as oxygen, nitrogen, etc. These heteroatoms exist in the form of acidic, basic or neutral organic functional groups [3-5]. Delocalised π electrons of aromatic rings and unsaturated valences also contribute to the basicity of carbonaceous sorbents.

Sometimes the original chemistry of the activated carbon surface is not potent enough to enhance the specific adsorbate-adsorbent interactions, in these cases the surface chemistry can be modified by the incorporation of heteroatoms such as nitrogen. The presence of nitrogen within the carbon matrix causes an increase in the number of basic groups, and changes the charge distribution in the graphene layers. Results published in the literature demonstrate the effect of nitrogen incorporation on the adsorptive properties of activated carbons for H_2S , SO_x , NO_x and acetaldehyde [6-9]. However, there are few studies dealing with the capture of CO_2 using active carbon [10].

On the other hand, there is a relevant environmentally unsustainable problem with the increasing amount of plastic waste. There is not a direct threat to the environment, but they pose a problem of considerable concern due to the huge amount of solid waste produced [11, 12]. Some works have been published on the obtention of active carbons from PET waste [13-15]. Besides the elimination of a residual plastic waste, the advantage afforded by the pyrolysis of post-consumer PET is that all the obtained sub-products exhibits interesting applications (i.e. chemical products, gases with a relatively high heating value and a solid that can be used as a valuable carbon material).

This work is situated in the context of minimising the impact of the huge amounts of residues generated from PET consumption. To this end, a series of nitrogen-enriched

carbons was obtained by mixing different nitrogen compounds (i.e., acridine, carbazole and urea) with PET waste, the latter constituting the carbon matrix. The originality of this work lays in the utilisation of a residue to obtain a valuable carbon material by introducing nitrogen (i.e., basic) functionalities in its composition. Thus, the target of this work was to deal with the problem of plastic disposal and recycling, and to assess the efficiency of the obtained adsorbents for an application of growing concern such as CO₂ capture. Thus, the approach included the synthesis of the carbon materials, their characterisation and the study of their CO₂ capture capacity as a function of temperature.

Experimental

Materials and procedures

PET from post-consumer soft-drink bottles was used as the carbon matrix for the prepared adsorbents. A series of compounds with different nitrogen functionalities, namely acridine, carbazole, and urea, supplied by Fisher, were used as source of nitrogen.

Chemical activation of the samples was performed by using KOH as the chemical reagent. The activation process involved the mixing of 1 g of PET with 1 g of the N-compound in a KOH solution containing 50 g of water. The concentration of the KOH solution was adjusted to give a chemical ratio of reagent to sample of 4:1. The mixing was performed at 85°C under stirring for 2 h.

After mixing, the slurry was subjected to vacuum-drying at 110°C overnight. The chemical-loaded samples were then carbonised in a horizontal cylindrical furnace in a N₂ atmosphere. Carbonisation was carried out by heating the samples at 30°C min⁻¹

from room temperature to 500°C, followed by holding the samples at the carbonisation temperature for 30 minutes.

After cooling under N₂, the carbonised products were washed by stirring with 250 ml of 0.5 N HCl solution at 85°C for 30 minutes, followed by filtration and washing in distilled water until pH 6. The final product was then dried in a vacuum at 110°C overnight, to give the final carbon adsorbents denoted as P (obtained from PET), P-A (obtained from PET with acridine), P-C (obtained from PET and carbazole) and P-U (obtained from PET and urea).

N₂ adsorption isotherms

Adsorption isotherms of N₂ at -196 °C were carried out in an ASAP 2010M from Micromeritics. Prior to the adsorption measurements the samples were outgassed at 300°C under high vacuum for 24 h. The surface areas and microporosity were calculated from the physical adsorption of N₂ using the BET and the Dubinin-Radushkevich equations, respectively [16].

CO₂ capture performance

The CO₂ capture and desorption performance of the prepared adsorbents was evaluated using a thermogravimetric analyser (TGA). Temperature-programmed adsorption tests were used in order to evaluate the influence of temperature upon the CO₂ capture capacity of the adsorbents. Approximately 10 mg of sample was placed in an alumina crucible and subjected to a drying process under N₂ at a gas flow rate of 20 ml min⁻¹. This entailed heating the sample at 20°C min⁻¹ to 100°C and then maintaining this temperature for 30 min. Subsequently, the temperature was decreased to room

temperature and the inert flowing gas was switched from N₂ to CO₂. This operating condition was maintained for 2 h and the weight increase was taken to be the CO₂ capture capacity of the materials at room temperature. Then the temperature was increased at 0.25°C min⁻¹ up to 100°C, and the weight change of the adsorbent was monitored to measure the capture capacity of the materials versus temperature. Finally, once the sample reached the final temperature (100°C), the gas was switched again from CO₂ to N₂ while the temperature was maintained at 100°C in order to determine the CO₂ desorption capacity of the samples.

Results and Discussion

Nitrogen content

The chemical characteristics of the activated samples are presented in Table 1. As expected, sample P contains no nitrogen. Taking into account that at 500°C (i.e., the carbonisation temperature) the N-compounds do not yield any residual char (see Figure 1), the fact that the final activated products contain, in some cases, large amounts of nitrogen indicates that secondary reactions and interactions have occurred during the carbonisation process, leading to the incorporation of nitrogen into the structure of the carbonised PET samples.

According to the N-contents presented in Table 1, carbazole is the N-compound from which the most nitrogen can be incorporated into the carbons (i.e., 4.2 wt% in daf basis), while the mixing with acridine and urea leads to adsorbents with the same nitrogen content (i.e., 0.5 wt% in daf basis).

Porous texture

Modifications with nitrogen-containing species may also result in changes in the porous structure. Table 2 summarises the structural parameters calculated from the N₂ adsorption isotherms such as the apparent BET surface area, the micropore volume evaluated from the DR equation, and the total pore volume (determined as the volume adsorbed at a relative pressure of 0.95). The samples modified with nitrogen-containing compounds presented lower apparent BET surface areas, as compared to the parent sample, P. This effect was significantly larger after modification with urea and acridine. The same changes were noticed in the total pore volumes.

These results suggest that the generation of porosity is influenced by the presence and nature of the nitrogen-enriched reagent used during the modification of the carbon matrix. Furthermore, it seems that the incorporation of nitrogen species to the edges of graphene layers may create steric hindrances and partially block the access of nitrogen to small pores.

The average size of pores also changed significantly upon the nitrogen-containing precursor, as reflected by the evaluation of the relative microporosity (W_o / V_{total}). It is interesting to note that the surface area and pore volume of the P-A sample are much smaller than those of P and P-C samples; however, its relative microporosity is similar to that in P and higher than P-C. In contrast, this parameter is minimum for P-U sample, indicating that modification with urea leads to the creation of pores of larger sizes.

CO₂ capture capacities

The capture capacities versus temperature of the adsorbents studied are presented in Figure 2. In this Figure the CO₂ uptake is expressed as the percentage of weight

increase during the capture tests. In all cases the highest capacity (i.e., highest weight uptake) occurred at room temperature, and a clear decrease was observed as the temperature increased. Furthermore, the process seems to be totally reversible, as the adsorbents return to their initial weight after switching the reactive gas (i.e., CO₂) to N₂ at the end of the experiment.

There are many factors that influence CO₂ capture, some of them are physical and some chemical. Textural properties are going to be determinant for any adsorption process but, in the case of CO₂ capture, chemical factors are also relevant. As CO₂ is an acid gas, the incorporation of nitrogen gives *a priori* a basic character to the adsorbent surface and promotes the CO₂ capture. Thus, as can be seen in Figure 2 the CO₂ capture profiles for the samples containing nitrogen appear over that of P. Furthermore, the major differences are observed between the capture capacities of P and P-C, either at room temperature or 100°C (see Table 3).

However, the amount of nitrogen incorporated to the carbon matrix is not the only factor influencing the CO₂ adsorption capacity. Consequently, the capture capacities were normalised with respect to several parameters. Thus, the weight uptake during the temperature-programmed CO₂ adsorption tests was normalised by the BET surface area of the adsorbent and the initial mass of the sample, giving a new parameter denoted as W_s . The variation of W_s with temperature is shown in Figure 3.

It can be observed that the capture capacity of the sample without nitrogen, P, is the lowest. However, it is worth to note that the sample with the highest amount of nitrogen (i.e., P-C) does not present the highest capture capacity of the samples studied. This indicates that not only the amount of nitrogen in the adsorbent is going to be important, but also the nitrogen functionality, as N-functionalities present different basicity [17].

In order to evaluate the activities of the different N-functionalities on CO₂ capture, the weight uptake during the temperature-programmed CO₂ adsorption tests was normalised by the surface area of the adsorbent, the nitrogen content and the initial mass of the sample, giving a new parameter denoted as $W_{S,N}$. The profiles obtained are presented in Figure 4. As these profiles are normalised by the surface area and nitrogen content, the different amounts of CO₂ uptake will depend on the nature of the nitrogen functionalities. The enhancement of the activity observed for N-doped materials is thought to be a consequence of the higher surface basicity. However, the activities found for the different nitrogenated species are different because they probably contribute in different ways to the basicity of the material. Interestingly, the sample obtained from the mixture of P and carbazole gives the higher N content in the adsorbent but it presents the lowest activity for CO₂ capture. On the other hand, the mixture with urea, that does not present a high N content, is the one with the most active/effective N-sites for CO₂ capture.

Conclusions

The series of nitrogen-enriched adsorbents, obtained by co-carbonisation of PET waste and N-compounds, showed a moderate effectivity for CO₂ capture. Carbon dioxide capture capacities of 4.8 wt% at room temperature and 1.2 wt% at 100°C were attained. In addition, from the comparison of the performance of the different adsorbents for CO₂ capture, it can be stated that not only the developed surface area and the N content are important, but also the nature of the N-functionalities. Further research is underway in order to promote the right N-functionality in the adsorbent for maximising CO₂ capture.

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Figure 1. Weight loss profiles during pyrolysis of PET and the nitrogen compounds used, in the thermobalance (A: Acridine, C: Carbazole, U: Urea).

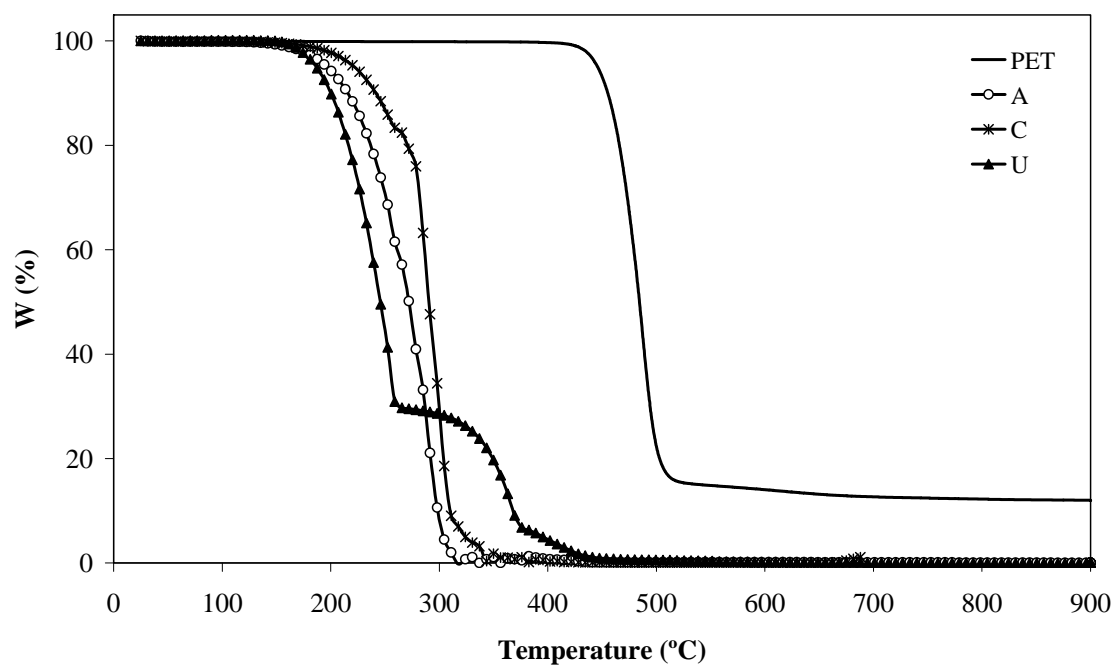


Figure 2. Percentage of weight uptake during temperature-programmed CO₂ capture/desorption profiles for the samples studied.

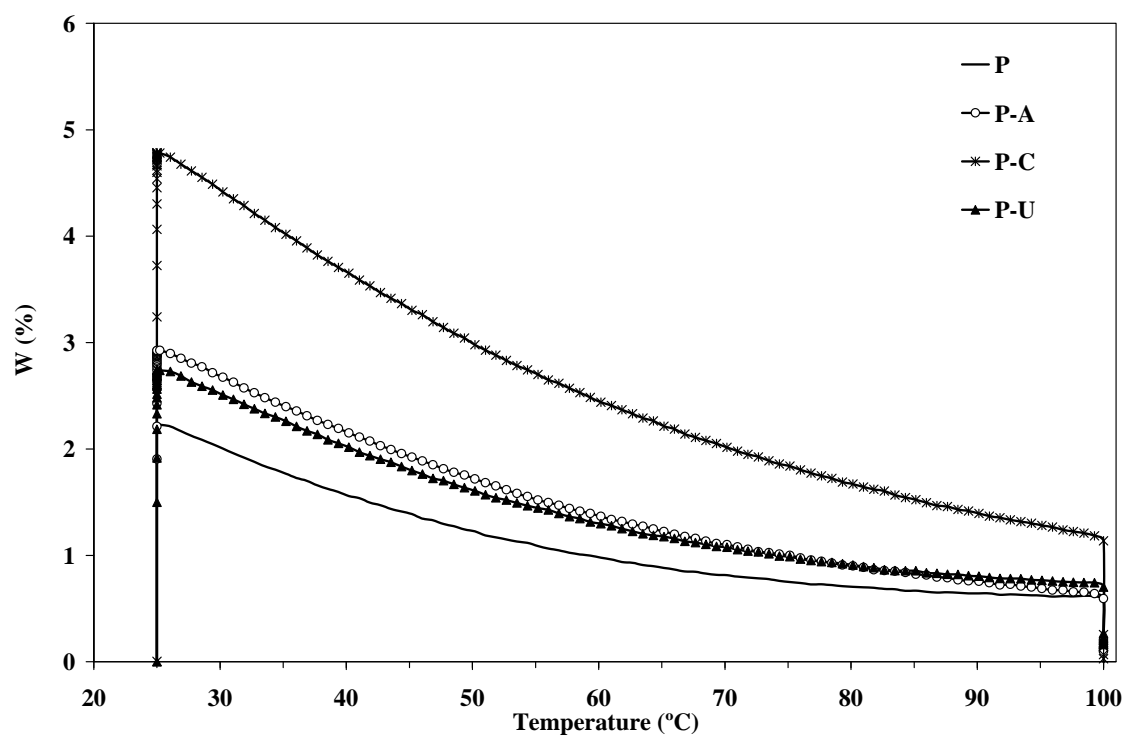


Figure 3. CO₂ uptake normalised by the surface area during temperature-programmed CO₂ capture/desorption profiles for the samples studied.

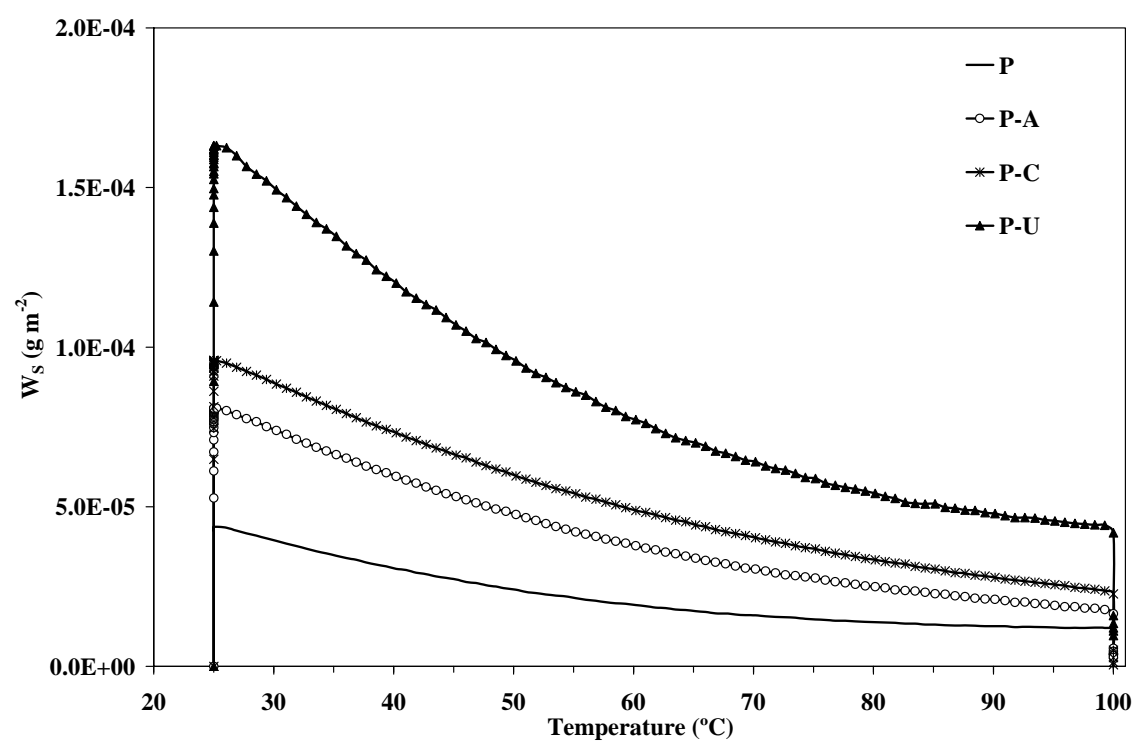
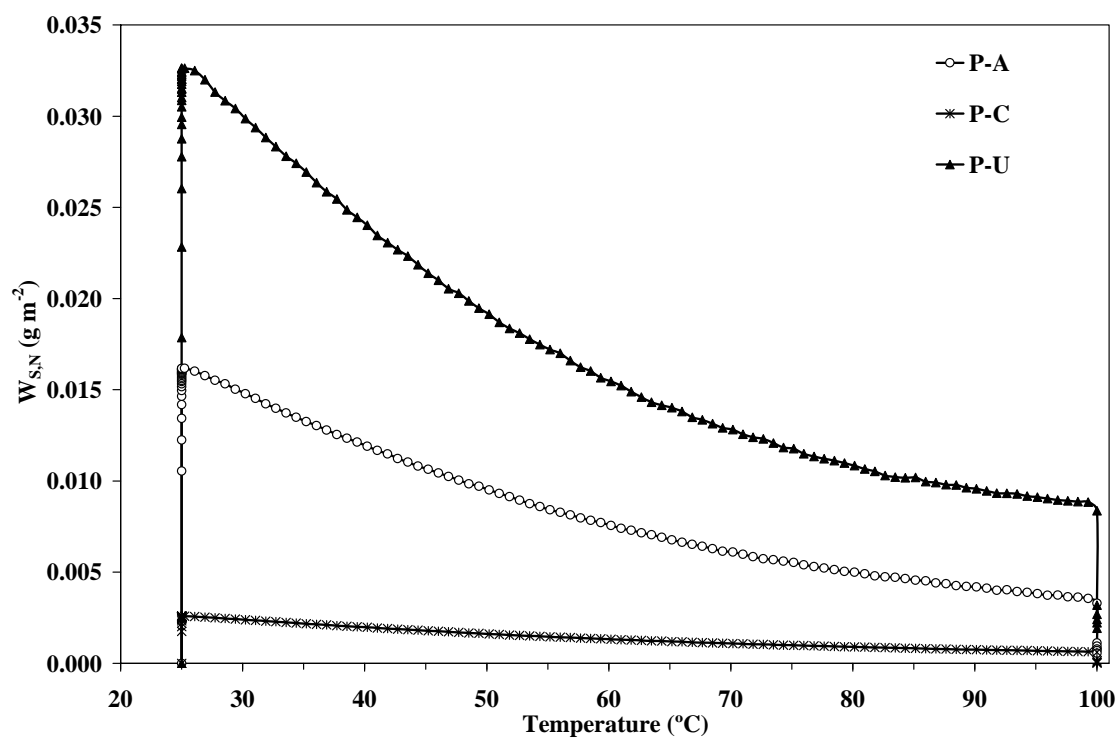


Figure 4. CO₂ uptake normalised by the surface area and nitrogen content during temperature-programmed CO₂ capture/desorption profiles for the samples studied.



Tables

Table 1. Ultimate analysis of the samples studied, in wt% dry ash free basis.

Sample	C	H	N	O	N/C atomic ratio $\times 10^{-3}$
P	81.3	2.7	-	16.0	-
P-A	73.7	3.1	0.5	22.7	6
P-C	75.2	2.8	4.2	17.8	47
P-U	75.2	2.6	0.5	21.7	6

Table 2. Textural parameters of the samples obtained from nitrogen adsorption isotherms at -196°C .

Sample	S_{BET}	C_{BET}	W_o (DR)	V_{total}	$V_{\text{micro}}/V_{\text{total}}$
P	472	789	0.188	0.209	0.90
P-A	318	442	0.136	0.152	0.90
P-C	418	415	0.169	0.202	0.84
P-U	150	355	0.063	0.092	0.69

Table 3. CO_2 capture capacities, in percentage of weight increase, at 25 and 100°C , of the adsorbents studied.

Sample	W (%) at $T = 25^{\circ}\text{C}$	W (%) at $T = 100^{\circ}\text{C}$
P	2.2	0.6
P-A	2.9	0.6
P-C	4.8	1.2
P-U	2.7	0.7